



Combustion Science Biofuels

Fundamentals of Biofuel Combustion Chemistry

As biofuels replace fossil fuels, the combustion chemistry must be optimized for tomorrow's engines.

Currently, 85% of the world's energy demand is met by the combustion of fossil fuels. The critical consequences of future supply shortages and environmental degradation (climate change and air pollution) have motivated many nations to transition away from conventional fuel sources and to instead utilize biofuels such as bio-ethanol, bio-butanol, and biodiesel. Biofuels offer the advantage of coming from large, mainly under-utilized biomass resources that are sustainable and renewable in a closed carbon cycle that reduces environmental impact.

Biofuels are already being blended with gasoline and diesel fuel for automotive and heavy-duty ground transportation. However, in order for biofuel combustion technology to evolve towards greater efficiency and reduced formation of harmful pollutants, a molecular-level

description of the combustion processes is necessary. From a chemical point of view, the typical biomass-derived fuel (alcohols, ethers, or esters) contains oxygen in its molecular structure; whereas, conventional hydrocarbon fossil fuels typically contain only carbon and hydrogen. While decades of combustion research have been performed on hydrocarbon fuels, investigations of the richer combustion chemistry of the oxygenated biofuels have only just begun.

Scientists at Sandia's Combustion Research Facility (supported by the Dept. of Energy, Office of Basic Energy Sciences) have collaborated over the past several months with colleagues at Cornell University and the University of Bielefeld in Germany to provide new insights into the complex reaction pathways associated with the combustion of biofuels. In their experimental work, mass spectrometry and laser-based techniques

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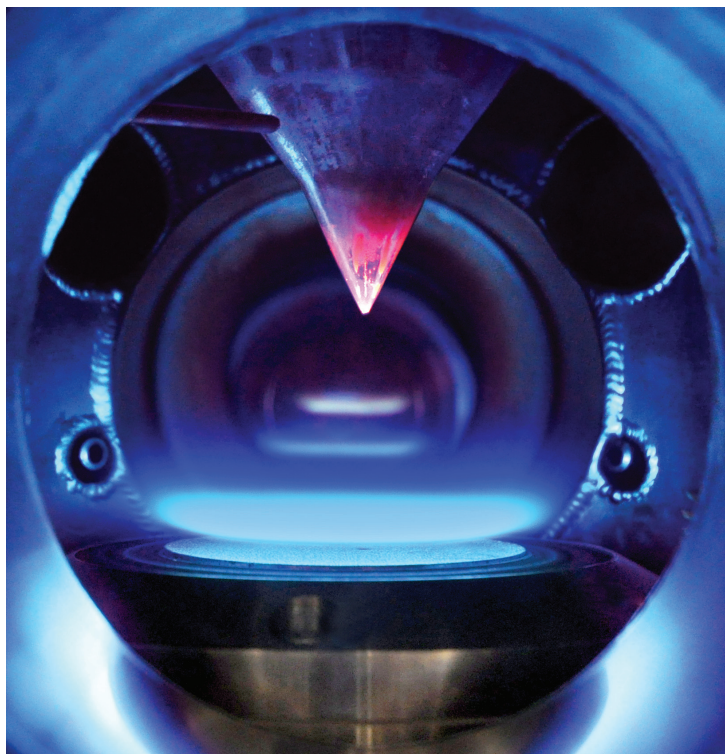



Figure 1: Flame analysis with photoionization molecular-beam mass spectrometry. Gases from a burner-stabilized flame (bottom) are sampled as a function of distance from the burner surface using a quartz cone (center), expanded into higher vacuum, and guided into the ionization chamber of a time-of-flight mass spectrometer for quantitative analysis.



are used to reveal the detailed chemical composition of laboratory-based model flames fueled by prototypical biofuel compounds. A photograph of such a model flame is shown in Figure 1. The flames are typically stabilized on a porous-plug burner at reduced pressure to widen the reaction zone where many of the intermediates are formed and consumed. Such a configuration ensures spatial homogeneity across the burner diameter and the combustion progress can be described in one dimension, i.e., as function of distance from the burner.

Exciting advances have been made possible in flame-sampling mass spectrometry experiments by employing tunable vacuum-ultraviolet photoionization at the Advanced Light Source (ALS) of Lawrence Berkeley National Laboratory (Reference 1). This sampling technique, combined with the mass spectrometric analysis, is the only viable detection method which provides selective and sensitive detection of all combustion intermediates simultaneously. Furthermore, the ALS-based experiment allows for the unambiguous detection of chemical compounds with the same empirical formula but different bond structures (i.e., isomers). Under identical conditions, isomers tend to react differently; therefore, isomer-resolving studies are of great value for the investigation of complex reactive environments as they yield a molecular-level description of the combustion chemistry. In order to develop such a step-by-step understanding of the entire combustion process, the experimental data sets are modeled using computer simulations in collaboration with Princeton University, North Carolina State University, and Lawrence Livermore National Laboratory.

In recent investigations, the influence of the chemical structure of biofuel molecules has been studied with respect to formation of intermediates and products, including pollutants. While the combustion chemistry of ethanol and dimethyl ether are relatively well understood, efforts are under way to unravel the important reaction steps in flames fueled by larger alcohols, such as propanol and butanol (Reference 2). From the results at hand, it might be inferred more generally that the combustion of oxygenated, bio-derived fuels would reduce the formation of soot and its precursors compared to the combustion of widely used fossil

fuels. Methods are also being developed to understand the mechanisms to describe the combustion chemistry of biodiesel fuels, which contain large methyl esters derived from a variety of vegetable oils and animal fats. However, largely because of the structural complexity of these large compounds, a molecular-level description of the respective combustion chemistry is still incomplete. Consequently, smaller, prototype methyl esters are being used as valuable steps towards a better understanding of the reaction pathways (Reference 2). The combustion chemistry of these small, prototypical methyl esters is not necessarily of direct practical relevance; however, any detailed combustion chemistry model describing their combustion behavior should be an important subset for predicting the combustion behavior of more realistic biodiesel compounds.

In conclusion, the chemical composition of transportation fuel is likely to change in the near future, with new biofuels already being established on the market. In order to make the most effective use of them, and to determine their emission characteristics, scientific research is under way to provide a detailed understanding of the underlying combustion chemistry.

References

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